DISSOCIATIVE EQUILIBRIUM AND PAIR GENERATION.*

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ABSTRACT.—A general formula for the dissociative equilibrium in an external radiation field is developed. This formula is applied to the phenomenon of thermal ionisation, and Saha's equation and other allied relations are obtained. It is further applied to the formation and annihilation of pairs of electrons and positrons existing in statistical equilibrium with radiation and the consequences are discussed.

INTRODUCTION.

The theory of dissociative equilibrium based upon thermodynamics was first given by Nernst in connection with molecular dissociation in a reversible chemical reaction and was further developed by Eggert [1] and Saha [2] in the field of atomic dissociation and applied to the study of internal and external constitution of stars respectively. In discussing Saha's formula, Russel [3] first suggested that external radiation may also play some part in ionisation. It is quite probable that an atom is not ionised by radiation alone but it is first excited to some higher state in which ionisation may come about more easily than in the unexcited state. Milne [4] also pointed out the same and Wood in fact demonstrated the existence of atoms in the excited states under the influence of radiation. These discussions led Saha [5] and Sur to investigate the effect of external radiation on ionisation equilibrium. Their result is however the same as obtained by Milne[6] from the study of statistical equilibrium in photo-electric effect.

Of late, the subject of equilibrium between matter and radiation has gained added importance on account of its connection with the conversion of matter into radiation and the reverse process which incidentally touches the question of the source of stellar energy and cosmic rays. The first successful theory in this direction has been given by Stern [7] who has deduced a relation for the concentration of matter that exists in equilibrium with radiation at a given temperature. The formulæ proposed by others from different considerations are essentially the same as Stern's. But the processes considered in the above theories do not include the mechanism of annihilation and regeneration of matter. The phenomena of annihilation and pair production have recently been discussed by

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Dirac [8] from the point of view of his Locher Theory and Heitler [9] on the basis of Dirac's idea has derived a relation again similar to that of Stern.

In the first part of this paper a general formula for the dissociative equilibrium is developed. This formula is applied to the ionisation equilibrium in the second part and the third part is devoted to the equilibrium involving the processes of annihilation and creation of pairs.

I.

Let C_κ and C_μ be the constituents of a reaction in equilibrium. These constituents may be particles of matter and quanta of energy. Let n_κ and n_μ be the units of C_κ and C_μ necessary for reaction. Also let this reaction be influenced by monochromatic external radiation. Then symbolically the reaction is given by

$$\Sigma n_\kappa C_\kappa + \text{Radiation} \rightleftharpoons \Sigma n_\mu C_\mu + \text{U} \quad \ldots \quad \ldots \quad (1)$$

Further from conservation of energy it follows that

$$\Sigma n_\kappa E_\kappa + h\nu \rightleftharpoons \Sigma n_\mu E_\mu + \text{U} \quad \ldots \quad \ldots \quad (2)$$

E_κ and E_μ are the total energies of the particles and U is the energy of transformation from the state k to μ. U may be positive or negative. For equilibrium evidently

$$\prod_\kappa \prod_\mu f_\kappa^{n_\kappa} (1 \pm f_\mu)^{n_\mu} f_\nu = \prod_\mu \prod_\kappa f_\mu^{n_\mu} (1 \pm f_\kappa)^{n_\kappa} (1 + f_\nu) \quad \ldots \quad (3)$$

where f_κ, f_μ f_ν are the distribution functions of the type of C_κ, C_μ and radiation and having energy E_κ, E_μ and $h\nu$ respectively. The left side gives the probability that n_κ units of C are converted into n_μ units of C_μ by absorbing $h\nu$. The right hand side gives the probability that n_μ is converted into n_κ by the emission of $h\nu$. The factors $(1 \pm f_\mu)$, $(1 \pm f_\kappa)$ and $(1 + f_\kappa)$ are introduced as customary in new statistics to allow for the preoccupiedness of the states into which the constituents of reaction are changing. Positive sign is used for the type governed by Bose-Einstein Statistics and negative sign for type governed by Fermi-Dirac Statistics.

$$\text{Now } f = \frac{1}{\frac{1}{A} e^{\frac{E}{kT}} \pm 1} \quad \ldots \quad \ldots \quad (4)$$

If C_κ and C_μ are material in nature obeying Fermi-Dirac Statistics the denominator of (4) will have positive sign and A is the degeneracy criterion of Sommerfeld. If they are particles of energy, obeying Bose statistics, the sign in the denominator is negative and A on account of indefinite numbers will not appear. Substituting the values of distribution functions from (4) in (3) and remembering (2) we obtain

$$\prod_{\mu}\prod_{\kappa} \frac{A_\mu^{n\mu}}{A_\kappa^{n\kappa}} = e^{\frac{h\nu}{k}\left(\frac{1}{T}-\frac{1}{T'}\right)-\frac{U}{kT}} \qquad \ldots \quad (5)$$

where T′ is the temperature of external radiation. The table below gives the value of A in the degenerate and non-degenerate states for the relativistic and non-relativistic systems.

	Non-relativistic $\frac{mc^2}{kT} >> 1$	Relativistic $\frac{mc^2}{kT} << 1$
Non-deg. $A << 1$	$A = \frac{nh^3}{G(2\pi mkT)^{\frac{3}{2}}}$	$A = \frac{n}{8\pi G}\left(\frac{ch}{kT}\right)^3$
Degenerate $A >> 1$	$\text{Log } A = \frac{h^2}{2mkT}\left(\frac{3n}{4\pi G}\right)^{\frac{2}{3}}$	$\text{Log } A = \frac{ch}{kT}\left(\frac{3n}{4\pi G}\right)^{\frac{1}{3}}$

G is the weight factor and mc^2 is the rest energy.

II.

IONISATION EQUILIBRIUM IN AN EXTERNAL RADIATION FIELD.*

The simplest type of this equilibrium is constituted by the atom of an element in the normal state existing along with its ionised atom free eletron and the external radiation. This may be expressed symbolically as

$$\text{Atom} + \text{Radiation} \rightleftharpoons \text{Ion} + \text{Electron} + \text{U}.$$

* Here and in the next section we shall discuss the equlibrium process only in the non-degenerate system. It is evident from the formulae given above that the process of dissociative equilibrium, discussed here, cannot take place in a degnerate system. [See reference (11)].

U is the ionisation potential. In this case C_κ is the atom, ΣC_μ correspond to ion and electron, $n_\kappa = 1$ and $n_\mu = 1$, when these values are substituted in (5) and also of A we get

$$\frac{N_i \cdot N_e}{N_a} = \frac{G_i . G_e (2\pi mekT)^{\frac{3}{2}}}{G_a h^3} \; e^{\frac{h\nu}{k}\left(\frac{1}{T} - \frac{1}{T'}\right) - \frac{U}{kT}}. \quad \ldots \quad (6)$$

In terms of partial pressure (6) is reduced to

$$\log \frac{P_i \cdot P_e}{P_a} \; \log \frac{G_i . G_e \; (2\pi me)^{\frac{3}{2}}}{G_a h^3} k^{\frac{5}{2}} + \tfrac{5}{2} \log T - \frac{U}{kT} + \frac{h\nu}{k}\left(\frac{1}{T} - \frac{1}{T'}\right) \quad \ldots \quad (7)$$

which is in fact the same as obtained by Einstein[10] from thermodynamic theory of Photo-Chemical Equivalence.

Since $e^{-\frac{h\nu}{kT}} = \dfrac{\rho_\nu}{\frac{8\pi h\nu^3}{c^3} + \rho_\nu}$ when ρ_ν is the energy density of radiation, relation (7) becomes

$$\log \frac{P_i \cdot P_e}{P_a} = \log \frac{G_i \cdot G_e (2\pi me)^{\frac{3}{2}}}{G_a h^3} k^{\frac{5}{2}} + \tfrac{5}{2} \log T + \frac{h\nu - U}{kT}$$

$$+ \log \frac{\rho_\nu}{\frac{8\pi h\nu^3}{c^3} + \rho_\nu} \quad \ldots \quad \ldots \quad (8)$$

This is the form of Saha[5] and Sur. A similar relation would follow from Milne.[6] In the absence of external radiation, (7) gives the well known Saha's formula for thermal ionisation—

$$\log \frac{P_i \cdot P_e}{P_d} = \log \frac{G_i \cdot G_e \; (2\pi me)^{\frac{3}{2}}}{G_a h^3} k^{\frac{5}{2}} + \tfrac{5}{2} \; \log T - \frac{U}{kT}. \quad \ldots \quad (9)$$

III.

EQUILIBRIUM BETWEEN MATTER AND RADIATION IN THE CASE OF ANNIHILATION AND FORMATION OF PAIRS.

When a particle of matter is converted into radiation at the same temperature as matter and the reverse process takes place, then for equilibrium we have

$$\text{Particle} \rightleftharpoons \text{Radiation}.$$

and $$E + mc^2 \rightleftharpoons h\nu.$$

Again from (5) by using the above two relations we get

$$\frac{1}{A_\rho} = e^{\frac{mc^2}{kT}} \quad \dots \quad \dots \quad \dots \quad (10)$$

since C_μ is the radiation, A_μ does not appear, $n_\mu = 1$, $n_\kappa = 1$, $A_\kappa = A_\rho$; $T = T'$ and $\mu = -mc^2$. Substituting for A_ρ in (10) we obtain

$$n_\rho = \frac{G_\rho \, (2\pi m_\rho \, kT)^{\frac{3}{2}}}{h^3} e^{-\frac{mc^2}{kT}} \quad \dots \quad (11)$$

which is Stern's formula.

For the annihilation of an atom of atomic number Z, which is already completely ionised, the equilibrium is given by

$$\text{nucleus} + \text{Z electrons} \rightleftharpoons \text{radiation}$$

and $$E_+ + M_+c^2 + ZE_- + Zm_-c^2 \rightleftharpoons h\nu$$

which reduce (5) to

$$\frac{1}{A_+} \frac{1}{A_-^Z} = e^{\frac{(M_+ + Zm_-)c^2}{kT}}$$

or

$$n_+ \, n_-^Z = G_+ G_-^Z \left\{ \left(\frac{(2\pi kT)_2}{h^3} \right)^{Z+1} (M_+ \; m_-^Z)^{\frac{3}{2}} \; e^{-\frac{(M_+ + Zm_-)c^2}{kT}} \right\}.$$

Since $n_+ = n_-$, the number of nuclei per unit volume

$$n_+ = \left\{ \frac{(2\pi kT)^{\frac{3}{2}}}{h^3} \left(M_+^{\frac{3}{2}} G_+ e^{-\frac{M_+c^2}{kT}} \right)^{\frac{1}{Z+1}} \left(m_-^{\frac{3}{2}} G_- e^{-\frac{m_-c^2}{kT}} \right)^{\frac{Z}{Z+1}} \right. \quad \dots \quad (12)$$

This relation was obtained by Kothari.[11] When applied to hydrogen it simplifies to give

$$n_+ = \frac{(2\pi kT)^{\frac{3}{2}}}{h^3} \left(G_+ M_+^{\frac{3}{2}} \; G_- m_-^{\frac{3}{2}} \right)^{\frac{1}{2}} e^{-\frac{(M_+ + m_-)c^2}{2kT}} \quad \dots \quad (13)$$

the formula of Kassel.[12]

As all these relations do not take us into the working of the process of annihilation we pass on to the Löcher Theory of Dirac. According to the relativistic theory both the positive and negative energy states of the electron are possible. Of these the most stable states for electrons will correspond to negative energy and high velocity, for in this case the energy is minimum. Such states will naturally be filled up by electrons obeying Pauli's Principle except perhaps a few associated with low velocity. But for these empty places or holes the whole region of negative energy state would remain unobservable. These holes (Löcher) are retarded in an external field of force as if they have charge $+e$ each and are identified with the so-called positrons. When an electron from a positive energy state jumps into the negative to fill one of the holes, an electron and a positron disappear simultaneously from the field giving rise to radiation. This is the phenomenon of annihilation. The energy evolved in the transition is equal to the difference of energies in the two states. The reverse process is the phenomenon of pair production. The conservations of charge and energy are fulfilled in these processes. But in order that the momentum may be conserved the annihilation should give rise to two quanta moving in the opposite directions. One quantum can however satisfy the momentum relation provided some nucleus or field is present to balance the excess of momentum. The protons and atoms may also annihilate if their counterparts (anti-protons and anti-atoms) are present in the negative energy states.

Thus we shall have

$$\text{Electron} + \text{Positron} \rightleftharpoons \text{Radiation}.$$
$$\text{Proton} + \text{Anti-proton} \rightleftharpoons \text{Radiation}.$$
$$\text{Atom} + \text{Anti-atom} \rightleftharpoons \text{Radiation}.$$

Solving for electrons and positrons from (5) we get

$$\frac{1}{A_+A_-} = e^{\frac{(m_+ + m_-)c^2}{kT}} \qquad \dots \qquad \dots \qquad \dots \quad (14)$$

or for the non-relativistic case

$$n_+n_- = \frac{(2\pi kT)^3}{h^6}\,(G_+m_+^{\frac{3}{2}}G_-m_-^{\frac{3}{2}})\,e^{-\frac{(m_+ + m_-)c^2}{kT}}$$

or since $n_+ = n_- = n$; $m_+ = m_- = m$ and $G_+ = G_- = G = 2$

$$n = \frac{G(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\frac{mc^2}{k\kappa}} \qquad \dots \qquad \dots \qquad \dots \quad (15)$$

and density $\rho = 2mn = \frac{2mG(2\pi mkT)^{\frac{3}{2}}}{h^3}\,e^{-\frac{mc^2}{kT}}$

or $$\log \rho = 12{\cdot}9 + \tfrac{3}{2} \log T - \frac{5{\cdot}9}{T} \times 10^{9}. \qquad \dots \qquad \dots \quad (16)$$

For the relativistic system where the energy of the pairs is much greater than the rest energy, (14) gives

$$n = 8\pi\, G \left(\frac{kT}{ch}\right)^{3} e^{-\frac{mc^2}{kT}} \qquad \dots \qquad \dots \quad (17)$$

Total energy of the system is given by

$$E = 3\,(2n)\,kT = \frac{48\pi\, G k^4 T^4}{c^3 h^3}\, e^{-\frac{mc^2}{kT}} \qquad \dots \qquad \dots \quad (18)$$

or as $mc^2/kT << 1$

$$E = \sigma'' T^4 \qquad \dots \qquad \dots \quad (19)$$

where $\sigma' = \dfrac{48\pi\, G k^4}{c^3 h^3}$, and

density $$\rho = \frac{E}{c^2} = \frac{48\pi\, G k^4}{c^5 h^3}\, T^4 \qquad \dots \qquad \dots \quad (20)$$

or $$\log \rho = \overline{35}{\cdot}2 + 4 \log T \qquad \dots \qquad \dots \quad (21)$$

Pressure of the system is equal to

$$P = \frac{E}{3} = \frac{16\pi\, G k^4}{c^3 h^3}\, T^4 = \tfrac{1}{3}\rho c^2 \qquad \dots \qquad \dots \quad (22)$$

The energy and the pressure in blackbody radiation on the other hand are given by

$$E = \sigma T^4 \text{ and } P = \frac{\sigma T^4}{3}$$

where $\sigma = \dfrac{8\pi^5 k^4}{15 c^3 h^3}$.

It is worth pointing out that when radiation is converted into matter or matter into radiation, the energy and pressure of the system increase or decrease respectively by the ratio $\frac{2 \times 90}{\pi^4} = 1{\cdot}8$. Thus when the formation of pairs takes place, the energy of the system is approximately double the blackbody radiation. This is what it should be as there is no difference between high speed particles and light quanta.

A curve reproduced in Fig. 1 is drawn to show the variation of density with temperature for the cases: (1) when the electrons are formed by pressure ionisation in which case they form degenerate gas, and (2) when the electrons are formed at the cost of radiation in pair generation. In the case (1) the density-temperature relation is given by $\rho >> 1{\cdot}7 \times 10^{-8}\, T^{\frac{3}{2}}$ for the non-relativistic case and the maximum value of density is less than $2{\cdot}10^{6}$ beyond which the system is relativistic and the density temperature relation is given by $\rho >> 6 \times 10^{-23}\, T^{3}$ The numerical values have been worked out for an ionised atom of iron. For case (2) the relation is given by formulae (16) and (21).

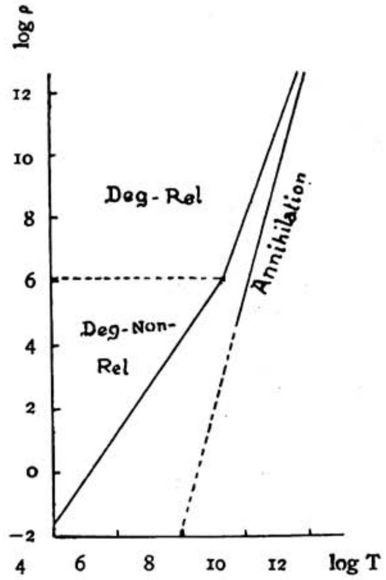

FIGURE 1.

It is observed from the graph that at density 10^5 and temperature 10^8 appreciable ionisation is only possible due to pressure ionisation. This happens in White Dwarf Stars. But to reach the same density in the equilibrium where pairs are being created or annihilated, the temperature of a higher order is required. Further it is evident from the definition of Polytropicindex $P = K\rho^{1+\frac{1}{n}}$ where P is the pressure, ρ is the density, n is the polytropicindex and K is a constant, that for stars built on the model of case (1) $n=3$ and $\frac{3}{2}$. Detailed investigations in these connections have been carried on by Eddington, Milne and others. For the case (2) we have $n=\infty$ and this gives rise to the model of stars having on isothermal core which has been studied by Emden.

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